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Vapour-Phase Carbonylation of Methanol over Tin Catalyst Supported on Active Carbon

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A Tin-active carbon showed a catalytic activity for the vapour phase carbonylation of methanol under pressurized conditions in the presence of methyl iodide promoter.

It is well-known that the carbonylation of methanol is catalyzed in the liquid phase by cobalt, rhodium, nickel, or iridium metal complexes.[1)] The reaction is also catalyzed in the vapour phase by zeolite or active carbon which carry the metals mentioned above.[2)] Main products of the reaction are methyl acetate and acetic acid. These authors have already reported[3-5)] that nickel on active carbon shows an excellent activity for the vapour phase carbonylation of methanol under mild conditions (250 °C, 11 atm). We have also studied the activity of active carbon supported group 8 metal catalysts.

In the present work, it was found that a tin catalyst which had never been known to show catalytic activity for carbonylation reaction, showed a high activity for the vapour phase carbonylation when it was supported on active carbon.

The catalyst precursors were obtained by impregnating a commercially available active-carbon (A.C.; Takeda Chemical, Shirasagi C, specific surface area 1200 m^2/g, particle size 20-40 mesh), SiO_2 (Fuji Davison, ID) or Al_2O_3 (Tokaikonetsu, TKS 99651) with metal chloride or acetate from aqueous solution by a dry-up method. They were reduced in a hydrogen stream, 400 °C, 3 h in situ before reaction. The metal loading was 2.5 wt% calculated as metal. The experimental apparatus and procedures are the same as in the preceding paper.[3)] Table 1 showed the experimental results over a variety of metals supported on A.C. The data in Table 1 were those at steady. All the metals supported on A.C. showed carbonylation activity.

Table 1. Carbonylation of methanol with supported catalysts[a)]

Catalyst	Yield /%					Select.[b)]
	AcOMe	AcOH	MeF	CH_4	DME	%
Ni/AC	60.1	25.7	0	1.1	4.5	93.9
Sn/AC	16.4	0.5	0.1	0.4	3.6	80.8
Sn/SiO_2	0	0	0	0.1	0.5	0
Sn/Al_2O_3	0	0	0	0.7	86.3	0
Mn/AC	8.8	0.1	0	1.1	7.8	50.0
Cu/AC	6.6	0	0	0.3	14.2	31.3
Cd/AC	4.7	0	0	0.3	15.4	23.0
Cr/AC	3.3	0	0.3	1.0	7.7	29.3
Re/AC	2.9	0.1	0.6	1.3	1.8	53.8
Se/AC	2.2	0	0	0.1	3.9	35.3
W/AC	1.7	0	0.2	0.7	4.4	27.4
V/AC	1.5	0	1.4	1.0	4.2	35.8
Ge/AC	1.3	0	0	0.1	3.5	26.3
Ga/AC	0.4	0	0	0.1	19.9	1.8
Zn/AC	0	0	0	0.1	27.5	0
AC	0	0	0	0	5.9	0

a)loading, 2.5 wt% as metal;
reaction condition, 250 °C, 11atm, W/F=5 g·h/mol;
feed, $CO/CH_3OH/CH_3I=100/19/1$ (molar ratio).
b)Selectivity to (AcOMe + AcOH).

Main products are methyl acetate (AcOMe) and dimethyl ether (DME). Minor products are acetic acid (AcOH), and methyl formate (MeF), methane (CH_4), and carbon dioxide (CO_2). Copper, Manganese and tin gave carbonylation products (AcOMe and AcOH) with the yield higher than 5%. While tin showed a high activity on A.C., tin supported on SiO_2 or Al_2O_3 gave no carbonylation products.

Figure 1 shows the product yields and carbonylation selectivity as a function of reaction temperature. AcOMe and AcOH yields increased as a rise in reaction temperature. In particular, the fraction of AcOH in the carbonylation products was high at high temperature. At the same time the yield of CH_4 increased markedly with rising temperature which caused the decrease of the carbonylation selectivity.

Figure 2 shows the activity change of an unreduced tin/A.C. catalyst. The activity increased proportionally to the time on stream whereas that of reduced catalyst reached a steady state soon after the reaction started. The phenomenon suggest that reduced tin is the active species of the methanol carbonylation.

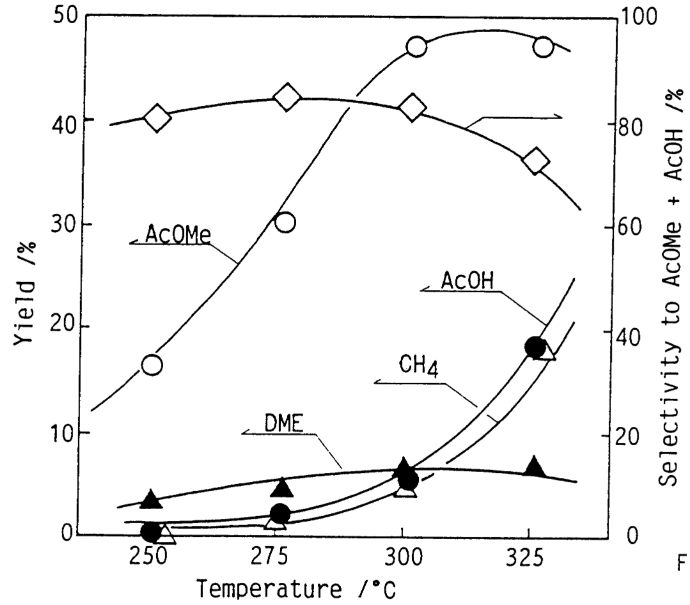

Fig.1. Effect of reaction temperature
Catalyst; Sn/A.C. (2.5 wt%)
Reaction conditions; 11 atm, W/F=5 g·h/mol, CO/MeOH/MeI=100/19/1 (molar ratio).

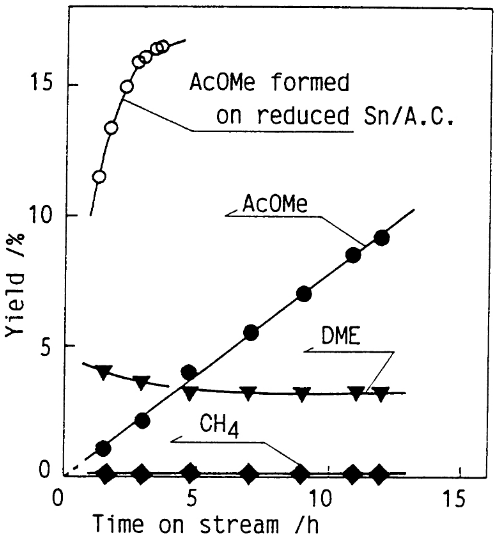

Fig.2. Activity change with process time
Catalyst; (●,▼,◆) unreduced Sn/A.C. (2.5 wt%)
(○) reduced Sn/A.C. (2.5 wt%)
Reaction conditions; 250 °C, 11 atm, W/F=5 g·h/mol, CO/MeOH/MeI=100/19/1 (molar ratio).

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